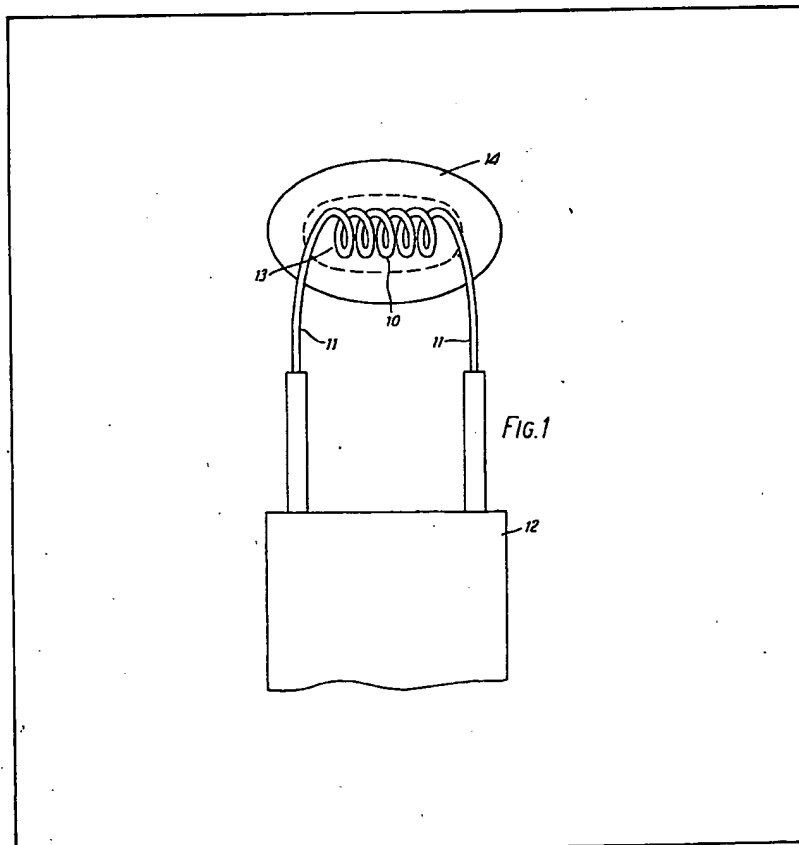


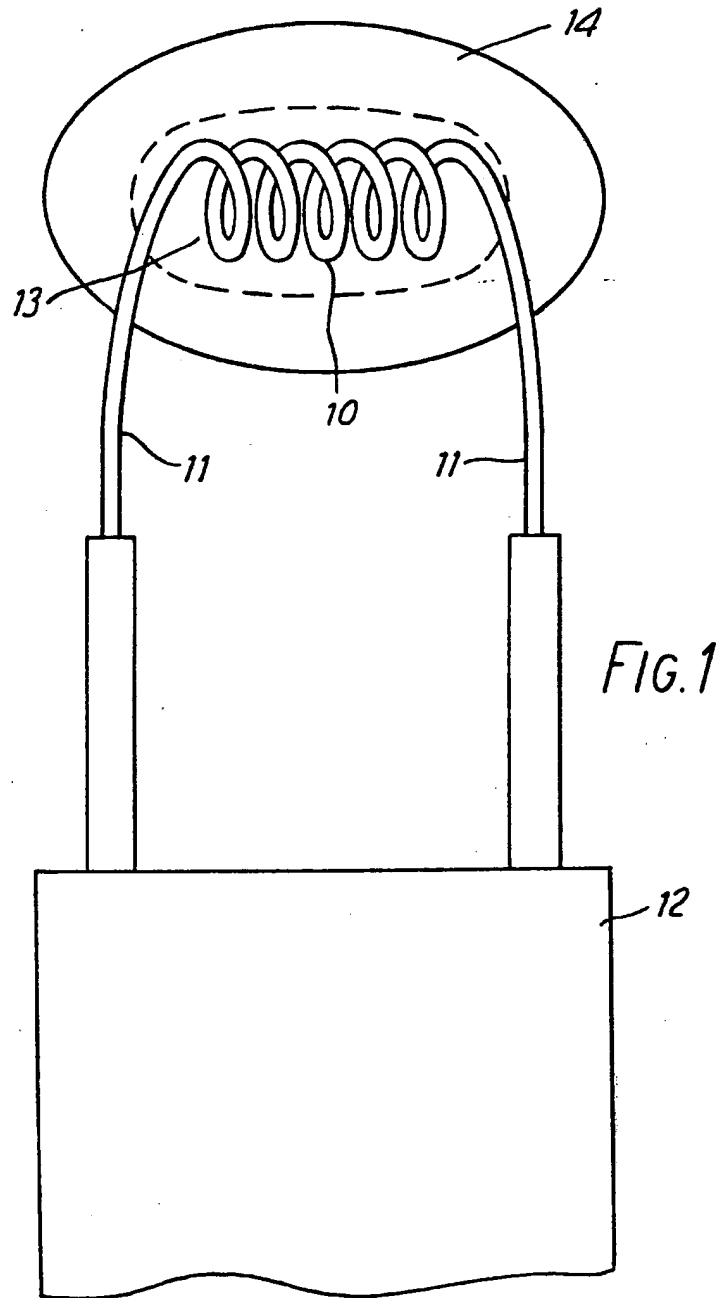
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**(54) Catalytic gas detector**

(57) A sensing element for a catalytic flammable gas detector comprises an electrically resistive heating element 10 of platinum wire coated with aluminium oxide 13 and embedded in a catalytic bead 14. The bead 14 consists of a precious metal catalyst and a metal oxide support. The previous metal catalyst is dispersed over the metal oxide support prior to the formation of the bead. The bead may also be formed with layers containing different catalysts. Before formation as a bead, a homogeneous mixture of the metal catalyst and the metal oxide support is obtained using filtration, evaporation and grinding techniques. Then several coats of a slurry of the supported catalyst powder are applied over the coated resistive element. Compensation for ambient temperature, pressure changes is provided by including the gas detector in a bridge in series with a resistor inert to the monitored gas.

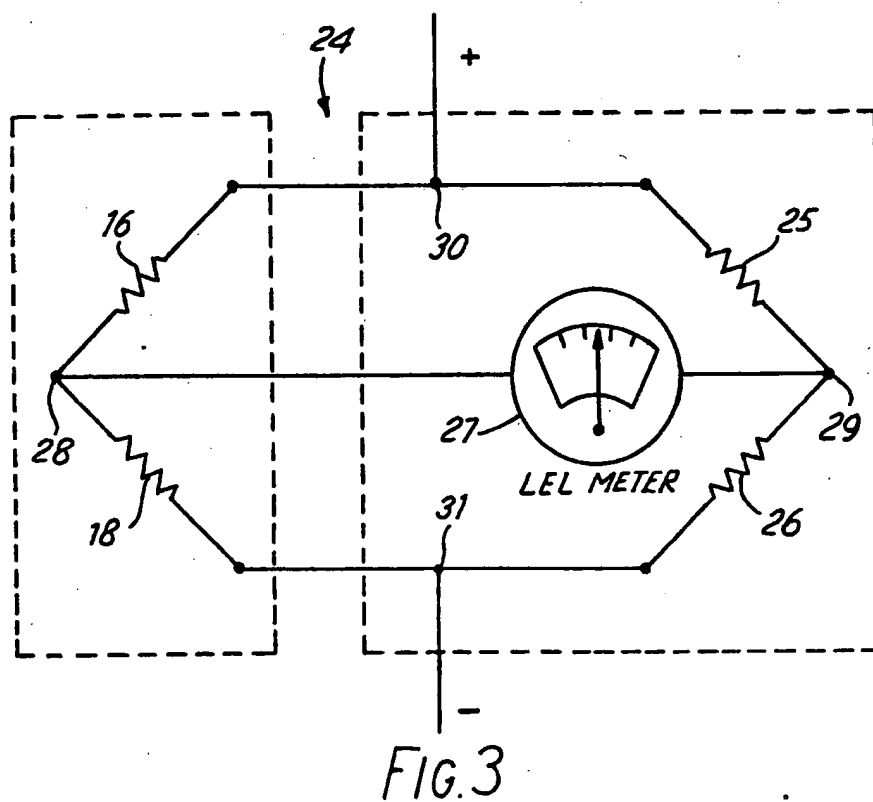
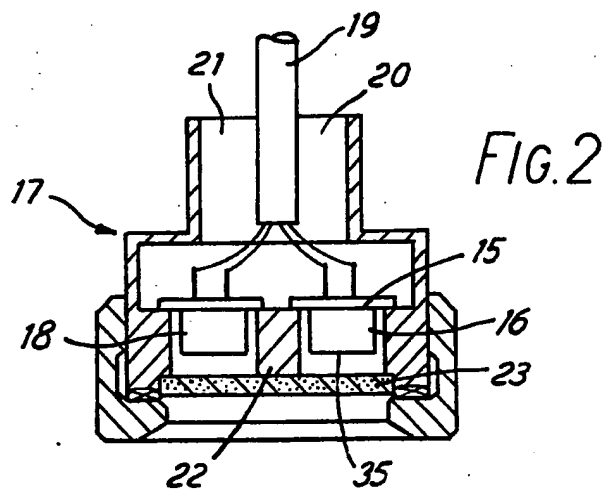


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## SPECIFICATION

## Catalytic gas detector

5 This invention relates to a flammable gas sensing element for use in a catalytic gas detector and to a method of manufacturing such elements.

Gas detectors which operate by catalytic combustion of flammable gases at the surface of a sensing  
10 element are well known. The sensing element usually comprises a platinum or a platinum alloy coil which is either wound round a silica former (see UK Patent No. 973250) or embedded in a refractory oxide bead (see UK Patent No. 892530), the constituents of which are  
15 thermally stable even on heating to temperatures as high as 750°C for long periods. A catalyst (normally a precious metal or precious metal oxide) which activates oxidation of flammable gases is dispersed over the support surface. The former device is known as a  
20 catalytic filament while the latter is known as a catalytic bead or "pellistor".

An electric current is passed through the coil to heat the bead to a temperature that is sufficient for total oxidation of the flammable gas reaching the surface of  
25 the bead. The current passed through the coil should be high enough to ensure that the output obtained from the bead is reasonably independent of small changes in temperature. The oxidation of the flammable gas is exothermic and therefore causes a rise in  
30 temperature on the surface of the catalyst which is transmitted through the support to the coil by conduction. A change in the electrical resistance of the coil results. This change in resistance is measured on a Wheatstone bridge, the bead being inserted into one  
35 arm of the bridge and the bridge being balanced when no flammable gases are present. The voltage developed across the bridge when a flammable gas is present is a measure of the concentration of the flammable gas.

40 A second bead is placed in another arm of the Wheatstone bridge to provide compensation for any changes in the voltage across the sensing bead caused by variation in ambient temperature or pressure. This second bead is normally called a non-sensitive or compensator bead and in previous gas  
45 detectors it has been constructed using a platinum wire coil coated with either a glass or an alumina bead. In the latter case, the surface is rendered inactive towards the flammable gas by treatment with potassium hydroxide.

To render them resistant to poisoning, catalytic beads have in the past been manufactured by a process which involves the deposition and the thermal decomposition of the precious metal salt on the  
55 support after it has been built into a bead. The thermal decomposition is normally achieved by electrical heating using the sensing coils. A disadvantage of such a technique lies in the fact that the temperature of decomposition of the bead cannot be controlled  
60 closely since the temperature of the surface of the catalytic bead cannot be measured accurately. Use of the Callendar equation ( $R_t = R_0 (1 + \alpha t + \beta t^2)$ ) where  $R_t$

and  $R_0$  are the resistance of temperature  $t$  and at 0°C respectively and  $\alpha$  and  $\beta$  are the first and second order  
65 coefficients of resistivity respectively) to calculate the heat produced by the coil is, at best, a crude approximation as the uniformity of heating throughout the coil is unknown as are the heat losses down the trail wires to the coil. Variations in the temperature,  
70 time and the gas atmosphere in which the decomposition takes place can affect the particle size of the catalyst. It is believed that a well dispersed catalyst containing fine particles is more resistant to poisoning than a poorly dispersed catalyst.

75 According to the present invention in a first aspect there is provided a sensing element for a catalytic flammable gas detector having an electrically heating element embedded in a bead comprising a precious metal catalyst and a metal oxide support, the metal  
80 catalyst having been dispersed over particles of the metal oxide support material prior to formation of the bead.

According to the present invention in a second aspect there is provided a method of making a sensing  
85 element for a catalytic gas detector in which a precious metal catalyst is dispersed over particles of a metal oxide support material and the supported catalyst is subsequently formed into a bead around an electrically resistive heating element.

90 The mean size of the supporting metal oxide particles should preferably be less than 100 nm and ideally less than 50 nm.

By heating the precious metal salt and support in an oven with a temperature controller, a batch of  
95 supported catalyst can be provided from which a number of beads of similar characteristics can be prepared. The particle size of the precious metal catalyst may also be controlled to a fine degree using this technique. For example platinum supported on  
100  $\gamma$ -alumina has particle diameters of 1 to 9 nm with an average diameter of 2.8 nm when prepared using this technique after calcination at 500°C. Palladium supported on  $\gamma$ -alumina has an average particle diameter of 13 nm after calcination at 500°C. On titania, the  
105 average particle sizes of the precious metals are 2.4 nm and 11 nm for platinum and palladium respectively. It is important that these dispersions of the precious metal achieved as the resistance to poisoning may often be related to particle size. A well dispersed  
110 catalyst containing fine particles is more resistant to chemical deactivation than a poorly dispersed catalyst because it presents more sites on which catalytic action can take place.

In addition to providing a consistent particle size,  
115 adsorption of the precious metal salt onto the support prior to construction of the bead allows the adsorption to be more closely controlled. The precious metal will be dispersed evenly throughout the support. This does not occur in the case of conventional beads  
120 where a concentration gradient exists, more precious metal being present in the outer layer of the bead. Adsorption of the catalyst prior to the formation of the bead ensures that the best use is made of the available surface of the support.

The drawing(s) originally filed was/were informal and the print here reproduced is taken from a later filed formal copy.

The technique of the present invention may be used to construct a bead having layers containing different catalysts. For example, an inner layer of supported palladium may be coated with an outer layer of supported platinum. The platinum layer is believed to be more resistant to poisons and protect the palladium layer beneath it.

The present invention thus consists of a bead constructed from a precious metal or metals dispersed over a support or supports of high surface area. The bead is constructed round a coil of wire which is used to heat the bead and to produce changes in voltage when a flammable gas is present. The catalyst is dispersed onto the support prior to the formation of a bead and the support is ground to provide a high surface area.

One method for carrying out the invention will now be described, by way of example, with reference to the accompanying drawings of which:

Figure 1 shows a catalytic bead;

Figure 2 shows a cross-section through a catalytic gas detector incorporating the catalytic bead of Figure 1; and

Figure 3 shows a Wheatstone Bridge circuit including the catalytic bead of Figure 1.

In constructing the bead of Figure 1 one may proceed as follows. A coil was constructed from platinum wire of 0.025mm diameter by winding 5½ times round a mandrel of 0.45mm diameter. The pitch of the turns was 0.125mm and the total length of the coil was 0.75mm. The trail wires 11 from the coil were welded onto a carrier 12 which was used to hold the coil rigid during subsequent processing. By means of electrical connections (not shown) to the carrier 12, the coil was heated to 200 mA to remove any contamination from the surface of the wire before dipping into a saturated aqueous solution of aluminium nitrate seventeen times. After each dip, the aluminium nitrate was thermally decomposed to aluminium oxide by passing a current of 220 mA through the coil for 10 seconds. In this way, the coil was completely covered with a coat of alumina which provided rigidity to the coil and a base 13 for the activated catalyst support 14.

The next stage involved the preparation of a supported catalyst powder. 200g of γ-aluminium oxide (manufactured by BDH Chemicals Limited) was ground for 30 hours in a ball mill grinder. Examination by scanning electron microscopy revealed that the particle size of the resulting powder was 40 - 80 nm. The powder was suspended in water and allowed to stand for five minutes. The larger particles, being heavier, fell to the bottom of the beaker while the smaller particles remained in suspension. The supernatant liquor was poured off and filtered to collect the smaller particles of alumina. The filtered residue was then dried in an oven at a temperature of 120°C.

A solution of 3g of palladium chloride in 30 ml of ammonia solution (specific gravity - 0.880) or 4.5g tetrammine palladium chloride in 30 ml water was stirred while 10g of the ground alumina prepared as above was slowly added. The resulting mixture was heated to boiling and allowed to reflux for 3 hours before allowing the water to be boiled off. The slurry was agitated using a plastic spatula during final

evaporation of the water to ensure an even distribution of the precious metal salt throughout the supporting alumina powder. The resulting yellow powder was ground in an agate pestle and mortar for 5 minutes to break up the large lumps before being transferred to a silica crucible and heated in an oven at 120°C for 2 hours to dry. The oven temperature was raised at 450°C for 16 hours to decompose the precious metal salt to palladium/palladium oxide. Finally, the supported catalyst powder was ground in an agate pestle and mortar for 5 minutes to give a finely divided brown powder.

A slurry was then prepared by adding 0.5g of the supported catalyst powder to 0.025g of aluminium nitrate and 0.7 mls distilled water and grinding for 5 minutes in an agate pestle and mortar. This slurry was applied to the alumina base 13 of the bead using a Pasteur pipette while passing a current of 25 mA through the coil to dry the slurry. 5 or 6 coats were normally sufficient to produce a bead of 1 mm diameter. After the final coat, the current through the coil is maintained at 25 mA for ten minutes before being ramped to 200 mA at a rate of 0.5 mA per second to decompose the aluminium nitrate into alumina so that it acts as a binder holding the palladium/palladium oxide catalyst on the alumina powder support together in a porous mass 14 on the base 13.

The bead was then ready for conditioning during which process it was exposed to a gaseous mixture containing 1.8% (v/v) methane in air at a current of 200 mA.

The bead was then mounted in a header 15 (see Fig. 2) and capped with a can 35. Instead of conditioning the bead before insertion the bead can be conditioned when mounted in the header can 35 but in this case the concentration of the methane should be increased to about 12% (v/v). The sensing element 16 thus formed was mounted in a metal body 17 alongside a compensating element 18 of similar construction to the element 16 except that the alumina support does not carry any catalyst and the compensating bead has been dipped in potassium hydroxide, zinc borate, or a mixture of zinc borate and chloro-auric acid to render it inert.

An electrical cable 19 providing electrical connections to the coils of the sensing element 16 and the compensating element 18, passes through an opening 20 in which it is sealed by an epoxy resin potting composition 21.

At the front of the body 17 there is an opening 22 which is covered with a sintered metal sieve 23 to prevent the heat generated by the catalytic combustion of flammable gas within the body 17 of the detector igniting the atmosphere outside the detector, whilst allowing atmosphere being monitored to diffuse into the body of the detector.

The sensing element 16 and the compensating element 18 are connected in series so that they form one arm of a conventional Wheatstone bridge circuit 24 (see Fig. 3). Two equal resistors 25 and 26 are connected in series to form the other arm of the bridge circuit 24. In the absence of an oxidation reaction on the sensing element 16 the bridge circuit 24 is balanced and no current flows through a current detector 27 connected between the midpoints 28 and

29 on the two arms of the circuit when a voltage is applied across the points 30 and 31.

Any changes in the ambient temperature or pressure is accompanied by corresponding changes in

5 resistance in the sensing and compensating elements so that the bridge remains balanced. However when oxidation of the flammable gas being detected occurs on the sensing element 16 causing its temperature to rise there is no corresponding change in temperature  
10 of the compensating element 18 because it is inert. The bridge 24 therefore becomes unbalanced so that current flows between the points 28 and 29 giving an indication on the current detecting device of the presence of the flammable gas in the atmosphere  
15 being monitored.

In the process described above the binder holding the supported catalyst powder together was aluminium (III) nitrate. Alternative binders that may be used are thorium (IV) nitrate, cerium (III) nitrate or organic  
20 binders such as polyvinyl acetate (PVA). The amount of binder used can be varied but for maximum resistance to chemical deactivation it is preferable to use as little binder as possible consistent with obtaining satisfactory binding of the support into the  
25 bead.

The catalyst used in the example was palladium.

Other catalysts that may be used include the precious metals platinum, rhodium and iridium or mixtures thereof. Furthermore a composite bead may be used  
30 consisting, for example, of an inner layer of palladium catalyst on an alumina support and an outer layer of platinum catalyst on an alumina support.

The metal oxide support in the example was alumina ( $\text{Al}_2\text{O}_3$ ), but other metal oxides or mixtures of  
35 metal oxides may be used including  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ThO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$  or  $\text{SnO}_2$ .

For example, thorium nitrate may be added to the suspension of alumina in the precious metal salt solution so that upon decomposition the finely  
40 divided catalyst support powder contains thoria as well as alumina.

Catalytic gas detectors can be constructed using the method described above, with greater consistency in quality from one sample to the next. This is due to the  
45 fact that many catalytic beads can be made from the same batch of prepared powder consisting of activated catalyst on the alumina or thoria support. The method also ensures that the catalyst is finely dispersed throughout the finished bead and it is  
50 believed that the decomposition of the catalyst can be more reliably controlled than when the decomposition takes place on the bead.

#### CLAIMS

1. A sensing element for a catalytic flammable gas  
55 detector comprising an electrically resistive heating element embedded in a bead having a precious metal catalyst and a metal oxide support, the metal catalyst having been dispersed over particles of the metal oxide support material prior to formation of the bead.

60 2. An element according to claim 1 in which the precious metal catalyst is a metal from group (VIII) of the Periodic Table.

3. An element according to claim 1 or 2 in which the heating element is a platinum or platinum alloy  
65 coil.

4. An element according to claim 1, 2 or 3 in which the precious metal and metal oxide support is applied over a layer of metal oxide free from precious metal catalyst on the heating element.

70 5. An element according to any of the preceding claims in which the metal oxide support of fine particle size is one or more of the following:  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ThO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{MnO}$ ,  $\text{SnO}_2$ .

6. A method of making a sensing element for a  
75 catalytic gas detector in which a precious metal catalyst dispersed over particles of a metal oxide support material and the supported catalyst is subsequently formed into a bead around an electrically resistive heating element.

80 7. A method according to claim 6 in which the heating element is a platinum or platinum alloy coil.

8. A method according to claim 6 or 7 in which the heating element is coated with a metal oxide layer prior to the formation of the bead.

85 9. A method according to claim 8 in which the metal oxide layer is formed by dipping the heating element in a solution of a metal salt and decomposing the metal salt to form its oxide.

10. A method according to any of claims 6 to 9 in  
90 which a precursor of the precious metal catalyst is mixed with the metal oxide support and heated to decompose the precursor into the precious metal and disperse it as fine particles in the metal oxide.

11. A method according to claim 10 in which a  
95 slurry is formed of metal oxide in a solution of a precious metal salt, the solution is filtered and the residue is heated to decompose the precious metal salt into the precious metal or its oxide.

12. A method according to claim 10 or 11 in which  
100 a salt of a metal different from the metal of the metal oxide support is mixed with the catalyst precursor before dispersion over the metal oxide support.

13. A method according to claim 12 in which the metal oxide is alumina and the salt is thorium nitrate.

105 14. A method according to any of claims 6 to 12 in which the metal oxide support is one or more of the following:  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ThO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{MgO}_2$  or  $\text{SnO}_2$ .

15. A method according to any of claims 6 to 14 in  
110 which the precious metal catalyst is one or more metals from group VIII of the Periodic Table.

16. A method according to any of claims 6 to 15 in which the bead is formed by making a slurry of the supported catalyst in a solution of a metal salt, coating  
115 the heating element with the slurry and allowing it to evaporate and heating the residue to decompose the metal salt to form a metal oxide binder.

17. A method according to claim 16 in which the metal salt is aluminium nitrate.

120 18. A method substantially as hereinbefore described with reference to the accompanying drawings.

19. A sensing element substantially as hereinbefore described with reference to the accompanying drawings.

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